I. RESTRICTED ROTATION IN NAPHTHYLAMINES
II. SYNTHESIS OF DECARBOXYLATED GOSSYPOLIC ACID

BY
ALFRED ANGELO ALBERT
B.S., Pennsylvania State College, 1938

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1942

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PART I

RESTRICTED ROTATION IN NAPHTHYLAMINES

Introduction

A study of several appropriately substituted anilines which exhibit optical activity due to restricted rotation about a carbon-nitrogen single covalent bond has been conducted in this laboratory[1,2] to compare the interference to rotation offered by various groups. The purpose of this investigation was to extend this work by the synthesis, resolution, and study of comparable naphthylamines.

Discussion of Results

Catalytic hydrogenation of 1-nitro-2-methylnaphthalene produced 1-amino-2-methylnaphthalene while reduction with stannous chloride and ethanolic hydrochloric acid yielded 1-amino-4-chloro-2-methylnaphthalene. The primary amines were treated with an alkyl sulfate to form the corresponding secondary amines which were then succinylated by means of succinic anhydride. The following compounds were synthesized in this manner: N-succinyl-1-methylamino-2-methylnaphthalene, N-succinyl-1-ethylamino-2-methylnaphthalene, and N-succinyl-1-methylamino-4-chloro-2-methylnaphthalene.

N-succinyl-1-methylamino-2-methylnaphthalene and N-succinyl-1-methylamino-4-chloro-2-methylnaphthalene were resolved through their quinine salts. The half-life period in boiling *n*-butanol of an active form of each was found to be 5.7 and 4.1 hours, respectively. Adams and Dankert[1] found the half-life period of N-succinyl-N-methyl-3-bromo-mesidine to be nine hours in boiling *n*-butanol. It was concluded, therefore, that the interference due to an aromatic —CH= group is less than that of a methyl group. These results are in agreement with those obtained from similar studies in the aryl olefin series.[3]

A salt of N-succinyl-1-ethylamino-2-methylnaphthalene suitable for resolution could not be found.

PART II

SYNTHESIS OF DECARBOXYLATED GOSSYPOLIC ACID

Introduction

Adams and coworkers[4] have assigned to gossypol the structure 2,2′-bi - (1,6,7 - trihydroxy-3-methyl- 5- isopropyl-8-aldehydonaphthyl). The only remaining point of uncertainty in this formulation is the relative positions of the binaphthyl linkage and the methyl groups. Decarboxylated gossypolic acid,[5] which is believed to be 4,4′-diisobutyryl-6,6′-dihydroxy-2,2′-dimethylbiphenyl, appears to be the simplest degradation product of gossypol through which this relationship may be determined. This investigation was concerned with the synthesis of decarboxylated gossypolic acid and thereby complete the study of the structure of gossypol.

Discussion of Results

The synthetic routes to decarboxylated gossypolic acid were chosen with consideration to previous attempts at its preparation.[6] None of the syntheses undertaken was ultimately successful.

The reduction of diazotized 4-amino-5-nitro-3-methylbenzoic acid failed to yield the expected biphenyl derivative. The amine was prepared from 4-amino-3-methylbenzoic acid[6] by acetylation, nitration, and subsequent hydrolysis.

The nitric acid oxidation of 2-nitro-3,5-dimethylanisole[2] resulted in the destruction of the molocule.

Copper bronze could not be caused to react with methyl 4-bromo-5-methoxy-3-methylbenzoate. This compound was synthesized from 4-bromo-5-nitro-3-methylbenzoic acid[7] by reduction to the amine, diazotization, hydrolysis of the diazonium salt, and simultaneous esterification and ether formation by means of dimethyl sulfate. A parallel route through the

intermediate methyl 4-iodo-5-nitro-3-methylbenzoate was abandoned because of the poor yield of this compound obtained by the nitration of methyl 4-iodo-3-methylbenzoate. The latter compound was obtained by the treatment of diazotized methyl 4-amino-3-methylbenzoate with aqueous potassium io-iodide solution.

The Ullmann reaction of methyl 4-bromo-5-nitro-3-methylbenzoate in nitrobenzene was successful in producing 4,4′-dicarbomethoxy-6,6′-dinitro-2,2′-dimethylbiphenyl. However, the desired dihydroxy compound could not be isolated from the product resulting from the hydrolysis of the tetrazonium salt of the corresponding diamine.

ADDENDUM

A New Technique For High Dilution Cyclization

An apparatus which permits the interaction of two bifunctional molecules at high dilution was designed and put into operation.

The reaction of hexamethylene diamine with hexamethylene diisocyanate at high dilution failed to yield any substance which could be proven to be the cyclic product of the interaction of one molecule of each reactant.

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VITA

The writer was born in Union City, New Jersey, on March 22, 1917. He received his elementary education in the public schools of the adjacent town of North Bergen and then attended Emerson High School of Union City from which he graduated in 1934. He entered Pennsylvania State College in the fall of that year and received the degree of Bachelor of Science in Chemistry from that institution in June, 1938. During his subsequent work in the Graduate School of the University of Illinois, he held appointments as Assistant in Chemistry from September, 1938, to June, 1941, and as Eastman Kodak Fellow for the year 1941-1942.

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